

12.—X-RAY ANALYSIS OF SOME TASMANIAN SOIL COLLOIDS,

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In a previous publication (1) the authors have described a technique developed in general for X-ray analysis of crystalline material in powdered form, and in particular for the investigation of soil colloids. In this paper an account is given of the application of the technique to the study of soil colloid fractions prepared and supplied by Mr. C. G. Stephens, Research Officer in the Waite Institute, Adelaide, South Australia, whose interest led the authors to undertake the X-ray investigation of these samples.

The following particulars with regard to (a) the location of the profile from which the soil samples were obtained, (b) the method of separation of the clay fractions, and (c) analytical data with respect to soil samples and clay samples were kindly supplied by Mr. Stephens.

(a) *Location*: All four colloid samples from soils 222, 499, 551 and 560 come from Tasmania. Samples 551 and 560 are soil colloid fractions from soils obtained from Illawarra about 12 miles from Launceston in northern Tasmania, and 499 is from the basaltic soils of north-west Tasmania. These three samples are soil colloid fractions of soils which failed to grow good subterranean clover with the usual dressing of superphosphate. 222 is a soil from the Huon Valley in southern Tasmania, and is typical of large areas of podsolie soils which, responding readily to superphosphate, grow good subterranean clover.

(b) *Method of Separation*: The method of separation employed by Mr. Stephens was prepared by Mr. C. S. Piper of the Waite Institute. In this method (which was adopted as giving a clay more suitable for silicate analysis) separation is made according to the former British system in which the clay fraction has a settling velocity of 8.6 cm. in 24 hours. This clay (1.4μ and less) is finer than "International clay" (2μ and less).

The soil is boiled in water and 5N NaCl solution is added. After standing the clear supernatant liquid is decanted and discarded. The sandy constituent is separated from the residue with a 90-mesh sieve and discarded. 5N NaCl is added to the residue. It is then decanted twice at suitable intervals being refilled with water after the first decantation. A solution of $\frac{1}{2}$ N Na_2CO_3 is added to effect dispersion. Successive decantations and refillings to a depth of 8.6 cm. at 24-hourly intervals then follow, the refillings being first with water, then with Na_2CO_3 solution and finally with water again. When all the clay has been collected it is treated with $\frac{1}{2}$ N acetic acid. 5N CaCl_2 is added to produce flocculation. After standing the clay is filtered and finally washed with alcohol and oven-dried.

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(c) *Analytical data relating to soil samples and clay fractions:—*

MECHANICAL AND CHEMICAL DATA OF THE SOILS.

—	222.	551.	560.	499.
	per cent.	per cent.	per cent.	per cent.
Coarse sand (2.0—0.2mm.)	13.5	23.5	25.2	2.9
Fine sand (0.2—0.02mm.)	36.1	19.5	21.6	9.6
Silt (0.02—0.002mm.)	25.7	26.4	20.5	14.9
Clay (less than 0.002mm.)	19.4	23.7	25.4	51.6
Loss on acid treatment	1.6	2.5	3.5	10.8
Moisture	1.1	0.8	0.6	1.7
Loss on ignition	6.1	8.5	8.9	19.7
CaO requirement to pH 7.0	0.20	0.24	0.21	0.70
N	0.23	0.20	0.40
P ₂ O ₅	0.14	0.16	0.15
K ₂ O	0.17
Reaction pH	5.1	5.8	5.7	5.4

CHEMICAL ANALYSIS AND MOLECULAR RATIOS OF CLAY FRACTIONS
(1.4 μ and less).

—	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{Fe}_2\text{O}_3}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Fe}_2\text{O}_3}$
	%	%	%				
222	65.6	25.8	4.3	3.9	4.3	0.09	41
551	63.7	23.1	9.4	3.7	4.7	0.26	18
560	53.1	29.8	12.8	2.4	3.0	0.28	11
499	35.0	36.2	22.2	1.2	1.7	0.39	4

X-RAY ANALYSIS.

For experimental details, for details of the method used for determining interplanar spacings from measurements on the film, and for accuracy of results reference may be made to the earlier publication.

Copper (filtered) radiation was used with all four samples. In the case of sample 499, on account of the high iron content, it was found necessary to use iron (unfiltered) radiation in order to reduce the intensity of the background on the film.

In Table I. are tabulated all observed values of d/n for clay fractions 222, 560 and 499. The powder photograph of 551 was almost identical with that of 560 and consequently the photograph of 560 only was analysed in detail.

Commonly occurring minerals in soil colloids include the clay minerals, quartz and the oxides and hydroxides of Al and of Fe.

The clay minerals are recognised by taking into account the fact that they may be divided into three groups, each group being characterised by a particular large spacing, the approximate value of which is in the case of—

- (1) the kaolinite group, 7 A;
- (2) the montmorillonite group, 14-15 A for the air-dried material;
and
- (3) the mica group, 10 A.

These lines are not subject to confusion by the proximity of any other lines. In the absence of a mica, quartz is characterised by a line at 3.34 A which is the strongest quartz diffraction line. The kaolinite group comprises kaolinite, anauxite, nacrite, dickite, halloysite and hydrous halloysite. The montmorillonite group comprises montmorillonite, beidellite, nontronite and saponite. No subdivision of the mica group is at present recognised. The minerals within a group cannot readily be distinguished in a diffraction pattern of a soil colloid. In the remainder of the paper the terms "kaolinite," "montmorillonite" and "mica" will be used, for brevity, to designate a mineral belonging to the kaolinite group, the montmorillonite group and the mica group respectively.

TABLE I.

Interplanar spacings of soil colloids and assigned origins. (Filtered Cu radiation with 222 and 560; unfiltered Fe radiation with 499).

222.			560.			499.		
Intens-ity.	d/n.	Possible Origin.	Intens-ity.	d/n.	Possible Origin.	Intens-ity.	d/n.	Possible Origin.
w	14.0	M	vw(?)	(¹)15 (?)	(M)	s	7.20	K
w	7.26	K	m	7.26	K	m	4.84	β line (²)
m	(³)4.54	MK	s	4.46	(M)	s	4.42	K
vs	4.15	KQ	s	4.05	KQ	s	4.12	K
m	3.72	?	w	3.66	?	m	3.54	K
s	3.32	Q	w	3.54	K	w	3.31	Q
w	2.57	MKQ	s	3.32	Q	vw	2.98	?
w	2.43		vw	2.66	H	d	2.80	H
w	2.34	K	d	2.56	(M)KQH	d	2.65	
w	2.27	KQ	d	2.41		d	2.55	KH
w	2.22		d	2.11		d	2.47	
vw	2.12	Q	w	1.96	KQ	d	2.31	?
w	1.97	KQ	vw	1.87	KH	d	2.17	
m	1.80	Q	m	1.80	Q	vw	1.97	K
d	1.65	MKQ	d	1.66	(M)KQH	w	1.82	H
m	1.53	Q	m	1.53	Q	d	1.67	KH
m	1.48	MK	m	1.48	(M)KH	vw	1.63	K
vw	1.44	KQ	vw	1.45	KQH	m	1.47	KH
m	1.37	Q	m	1.37	Q	d	1.44	H
vw	1.32	K	vw	1.32	K	d	1.41	
vw	1.28	MQ	vw	1.27	(M)Q
d	1.23	MKQ	d	1.23	(M)KQ
w	1.20	Q	vw	1.19	Q
w	1.17	Q		1.17	
vw	1.14	Q	vw	1.14	Q
vw	1.07	Q	vw	1.07	Q
vw	1.04	Q
vw	1.01	Q
vw	0.91	Q
vw	0.88	Q

vs = very strong ; s = strong ; m = medium ; w = weak ; vw = very weak ; d = diffuse.

M = Montmorillonite ; K = Kaolinite ; Q = Quartz ; H = Haematite.

(1) A faint suggestion only of this line appears. Not confirmed by heat treatment.

(2) The value of d/n obtained on the assumption that this is the β line is 4.39A.

(3) This is the inner edge of a line that extends to the next line centred at 4.15A.

Brackets imply measurements of the inside and outside edges of a broad line (or lines).

The two unidentified lines in 499 could be associated with medium lines in the diffraction pattern of a mica. This is not inconsistent with the rest of the observed pattern of 499. The absence of the characteristic mica line has already been referred to.

On the basis of these characteristic lines, 222 was found to contain quartz, kaolinite and montmorillonite; 551 and 560 contain quartz and kaolinite with a possible trace of montmorillonite; 499 contains quartz and kaolinite. On the same basis there was no evidence of the existence of a mineral of the mica group in any of the clay samples.

In the previous Table I. are listed all the recorded lines for each clay sample with the assigned origin for each line. The data relating to the clays and to quartz were taken from Nagelschmidt (*Zeit. f. Krist.*, 87, 120, 1934) and from Favajee (*id.* 100, 425, 1939). Where a recorded line could be identified with a line of medium or higher intensity as listed in the published data, a line with the same spacing in the pattern of another mineral was neglected when its intensity was less than medium.

The recorded lines were also examined with a view to obtaining evidence of the existence or non-existence of any of the oxides and hydroxides of Al and of Fe. For this purpose data supplied by Hanawalt, Rinn and Frevel (*Ind. & Eng. Chem., Anal. Ed.*, 10, 457, 1938) was used. The only mineral of this group whose existence could be established was haematite. The four strongest haematite lines in order of decreasing intensity are 2.69 Å, 2.51 Å and (of equal intensity) 1.84 Å and 1.69 Å. Haematite is presumed to be present in samples 560, 551 and 499. No quartz or clay lines occur in the vicinity of 2.69 Å. The strongest gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) *line occurs at 4.88 Å. In sample 499 a line appears at 4.84 Å (assigned in Table I. to β radiation). From intensity considerations one cannot exclude the possibility of gibbsite being present in small quantity in this sample. From the X-ray evidence no opinion could be arrived at with regard to the presence or absence of any other mineral of this group. A magnetic test with an electro-magnet indicated the existence of a weakly magnetic material in the above three clay samples.

In Table II. are summarised the final conclusions with regard to the composition of the clay fractions. All estimates of relative quantities of the different constituents are based on visual observation of line intensities. These estimated relative quantities may correctly indicate the actual relative quantities only if the ratio of the intensities of patterns of different constituents is equal to the ratio of the proportions of the constituents. This may not be true and may depart widely from the truth if quartz is one of the constituents since the diffracting power of quartz is markedly greater than that of any other clay mineral.

With a view to obtaining more evidence as to the existence or non-existence of any montmorillonite in 560 (and 551), 560 was heated in a furnace in air for a day at 500° C. The 15 Å spacing of montmorillonite shrinks to 10 Å as a result of such treatment. No trace of such a line was observed. The main effect upon the pattern was in accord with the almost complete destruction of kaolinite. Other effects noted were, firstly, the appearance of a broad diffuse line centring at about 5.2 Å resembling a diffraction ring from a non-crystalline material. There is a faint trace of this "diffraction ring" in the pattern of 499, and perhaps also (but still fainter) in the patterns of the

* The diffraction pattern given by Hanawalt *et al.* and assigned by them to "bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)" agrees closely with the diffraction pattern assigned by Nagelschmidt (*Journ. Agri. Sci.* Vol. **xxix**, 490, 1939) to gibbsite. We have followed Nagelschmidt in this.

TABLE II.
Composition of the soil colloids.

Fraction.				Quartz.	Kaolinite.	Montmorillonite.	Haematite.
222	Much	Little	Little	...
551	↑ Much	Much	Possible trace	Very little
560	↑ Much	Much	Possible trace	Very little
499	Very little	Much	...	Little

Note:

(1) An arrow (\rightarrow) indicates increasing amounts of quartz. A similar assessment with regard to kaolinite in 551, 560 and 499 could not be made.

(2) The possibility of the presence of gibbsite in 499 cannot be excluded.

other clay fractions, including that of unheated 560. Secondly, a prominent new line appeared at 3.74 Å. This line appears in the pattern of 222. It has also been observed on another occasion (1) where it might be attributable to a decomposition product of kaolinite which the authors have not been able to identify.

A microscopic examination has been made and results will be published separately.

SUMMARY.

An X-ray analysis of four clay fractions (effective diameter 1.4μ and less) separated from four different Tasmanian soil samples is described. Results appear in Table II.

Results of a microscopic examination will be published separately.

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Our thanks are also due to Mr. C. G. Stephens, Research Officer in the Waite Institute, South Australia.

REFERENCE.

(1) Shearer, J., and Cole, W. F., Jour. Roy. Soc. W.A., 1939-40, Vol. xxvi., pp. 121-131.

